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13. ABSTRACT (Maximum 200 words) A variety of Air Force applications require highly detailed information about atoms, molecules, and their interactions. This information is necessary in problems ranging from chemical laser development, to the detection and identification of rocket plumes, to non-linear optics electron beam technology, and high density and energy fuels. The crucial component needed to understand molecular reactions is the potential energy surfaces (PES) that serve to describe the attractions among the atoms and molecules. However, such information is not easy to obtain. In many cases, the most direct approach to obtaining accurate potential surfaces for molecules, and detailed information about their excited states, vibrational spectra, and a wealth of other quantities, is high level ab initio solutions of the Schrodinger equation.			
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**Final Report**  
**Molecular Interactions and**  
**Properties with Many-Body Methods**

**AFOSR-90-0079**

**to**

**Air Force Office of Scientific Research**

**Rodney J. Bartlett**  
**Quantum Theory Project**  
**University of Florida**  
**Gainesville, Florida 32611**

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## I. Introduction

A variety of Air Force applications require highly detailed information about atoms, molecules, and their interactions. This information is necessary in problems ranging from chemical laser development, to the detection and identification of rocket plumes, to non-linear optics, electron beam technology, and high density and energy fuels.

The crucial component needed to understand molecular reactions is the potential energy surfaces (PES) that serve to describe the attractions among the atoms and molecules. However, such information is not easy to obtain. In many cases, the most direct approach to obtaining accurate potential surfaces for molecules, and detailed information about their excited states, vibrational spectra, and a wealth of other quantities, is high level *ab initio* solutions of the Schrödinger equation.

However, more so than in most other areas, the ability to provide reliable quantum mechanical results for increasingly large molecules depends critically on improved method development. Whereas supercomputers can enable us to make much larger computations with old methods, the simultaneous development of new methods can increase computational capability by further orders of magnitude. In this regard, many-body perturbation theory (MBPT) and its infinite-order extensions termed coupled-cluster (CC) methods offer a number of attractive features that the more traditional configuration interaction approaches lack.

Under AFOSR support, we have established these CC/MBPT theories as being among the most accurate available, and have developed very efficient and generally applicable computer programs to perform CC/MBPT calculations. Also, we have employed these methods for the first time in large-scale *ab initio* calculations of potential energy surfaces. The successes of our original work in this effort have been substantial (see previous AFOSR reports).

Following a statement of research objectives, we review the recent scientific advances we have made under AFOSR support.

## II. Research Objectives

The overall objective of our continuing research program for AFOSR has included the following:

1. The development of new, more accurate and more efficient *ab initio* quantum mechanical methods based upon coupled-cluster (CC) and many-body perturbation theory (MBPT) for determining molecular properties and potential energy surfaces for molecular interactions.
2. The implementation of these methods into highly efficient, transportable computer programs (ACES II), to enable computations on molecules to be made on an almost routine basis, for a wide variety of different properties.
3. The application of these techniques to a variety of problems that are of interest to AFOSR, and that serve to establish the range of accuracy for CC/MBPT methods.

The underlying goal of our effort is highly accurate first principle quantum mechanical predictions of molecular properties. Such tools are already making possible the determination of dissociation energies, moments, polarizabilities, excitation energies, and vibrational and

rotational spectra for molecules to an accuracy that is predictive and comparable to experiment. Furthermore, for transient molecules as occur in rocket plumes, combustion, flame chemistry, and interstellar space that are generally difficult to study experimentally, theoretical calculations will provide otherwise inaccessible information. In addition, theoretical work provides the underlying framework to understand innumerable important molecular phenomena and to suggest previously unanticipated solutions to defense related problems. All of the new methods which we develop are being incorporated into our Advanced Concepts in Electronic Structure II (ACES II) program system. The program has been established at Air Force installations for use by other Air Force researchers.

### III. Notable Accomplishments This Past Year

- A. A primary achievement of this past year is the implementation and application of the full CCSDTQ method for several molecules.<sup>4\*</sup> Such a method, which includes the connected  $T_4$  cluster, in addition to  $T_1$ ,  $T_2$  and  $T_3$  is exact for four-electron systems, and through four-electron clusters in many electron molecules; and is correct through sixth-order in perturbation theory. We introduced fully factorized equations using the recursive generation of intermediate approach we recently developed. Hence, despite the highly non-linear nature of the CCSD(T) equations, all operations only involve multiplication of an integral with a single  $t$  amplitude. Compared to full CI, the average errors for CCSDTQ are 14  $\mu$ hartrees at equilibrium geometries and 26  $\mu$ hartrees at twice  $R_e$ .
- B. Another notable achievement this year was our report of the first, open-shell MBPT(2) analytical second derivative (Hessian) method.<sup>2</sup> For unrestricted Hartree-Fock (UHF) references, we developed a general purpose program and added it to our ACES II program system. We report results for force constants and vibrational frequencies for the interesting  $CF_2$  molecule in its triplet state.
- C. The ketenyl radical  $HC=C=O$  plays a role in a number of important reactions, such as those involving acetylene and oxygen and it occurs in interstellar space. It exhibits a Renner-Teller splitting, causing it to be bent in its ground state, but its detailed structure and vibrational frequencies are unknown. We provide predictions<sup>3</sup> using our recently developed analytical gradient CC methods. As the problem is complicated by symmetry breaking, careful use of symmetry adapted coordinates are required to obtain second derivatives.
- D. Another advance this year was the first development of open-shell analytical coupled cluster gradients for methods that include triple excitations.<sup>8</sup> We developed the equations and implemented into ACES II analytical derivative methods for MBPT(4), CCSD+T(CCSD), CCSD(T) and QCISD(T) with a UHF open-shell reference. The primary application was to the important atmospheric radical, HOO. Structures and vibrational frequencies were obtained at several levels of approximation.
- E. In a similar study, we generalized the analytical gradient theory for triple excitation methods to use a restricted open-shell Hartree-Fock (ROHF) reference function.<sup>9</sup> Several examples including comparison with full CI are reported.

\* References in this section refer to the AFOSR publication list on p. 5.

- F. In our continuing efforts toward defining the best non-iterative higher-order correlation corrections we studied several examples where full CI results are available (BH, HF, H<sub>2</sub>O). We used the non-iterative triples model CCSD+T(CCSD), triples and quads, CCSD+TQ\*(CCSD), and the CCSDT+Q(CCSDT), non-iterative quads augmented CCSDT method, plus several new methods.<sup>10</sup> Even in regions of approaching severe degeneracy, where a multi-reference method would be strongly preferred, the higher-level single reference, non-iterative methods CCSD+TQ\*(CCSD) and CCSDT+Q(CCSDT) were found to perform exceptionally well, comparing favorably with reference full CI results.
- G. Like the UHF-MBPT(2) open-shell second derivative method, another substantial achievement was deriving and implementing analytical MBPT(2) second derivatives for the restricted open-shell Hartree Fock (ROHF) based MBPT method.<sup>7</sup> Unlike UHF, ROHF provides a wavefunction which is a spin eigenfunction. This makes it possible to get much improved results for cases where UHF has a large degree of spin contamination. Our illustrative example was for the methylimidogen (CH<sub>2</sub>N) radical, which is strongly spin contaminated. ROHF-MBPT(2) gives much better vibrational frequencies compared to UHF-MBPT(2). As ROHF MBPT requires the development of a new MBPT method, analytical second derivatives represent a major accomplishment and its presence in ACES II guarantees wide application.
- H. Finally, we address some formal questions concerning the nature of energy functionals and the appropriateness of various alternative ansätze in CC theory.<sup>5,11</sup> We consider unitary (UCC), expectation value (XCC), and the extended (ECC) method, and their satisfaction of several desiderata. Only ECC satisfies all requirements, but it is prohibitively difficult to apply. We find that standard CC methods are difficult to top for realistic applications.

All of the above are important, timely developments in the field that provide solutions to molecular problems that in many cases, could not be previously addressed.

#### IV. Publications Supported by AFOSR (1992)

1. J.F. Stanton, J. Gauss and R.J. Bartlett, "On the Choice of Orbitals for Symmetry Breaking Problems with Application to  $\text{NO}_3$ ," *J. Chem. Phys.* **97**, 5554 (1992).
2. J.F. Stanton, J. Gauss and R.J. Bartlett, "Analytic Evaluation of Second Derivatives Using Second-Order Many-Body Perturbation Theory and Unrestricted Hartree-Fock Reference Functions," *Chem. Phys. Lett.* **195**, 194 (1992).
3. P.G. Szalay, J.F. Stanton and R.J. Bartlett, "A Systematic Coupled-Cluster Investigation of Structure and Vibrational Frequencies of the Lowest Electronic States of Ketenyl Radical," *Chem. Phys. Lett.* **193**, 573 (1992).
4. S.A. Kucharski and R.J. Bartlett, "The Coupled-Cluster Single, Double, Triple and Quadruple Excitation Method," *J. Chem. Phys.* **97**, 4282 (1992).
5. P.G. Szalay and R.J. Bartlett, "Alternative Ansätze in Coupled-Cluster Theory IV. Comparison for the Two Electron Problem and the Rôle of Exclusion Principle Violating (EPV) Terms," *Int. J. Quantum Chem.* **S26**, 85 (1992).
6. J.F. Stanton, J. Gauss, J.D. Watts, W.J. Lauderdale and R.J. Bartlett, "The Aces II Program System," *Int. J. Quantum Chem.* **S26**, 879 (1992).
7. J. Gauss, J.F. Stanton and R.J. Bartlett, "Analytic Restricted Open-shell Hartree-Fock-Many-Body Perturbation Theory(2) Second Derivatives," *J. Chem. Phys.* **97**, 7825 (1992).
8. J.D. Watts, J. Gauss and R.J. Bartlett, "Open-Shell Analytical Energy Gradients, for Triple Excitation Many-Body, Coupled-Cluster Methods: MBPT(4), CCSD+T(CCSD), CCSD(T), and QCISD(T)," *Chem. Phys. Lett.* **200**, 1 (1992).
9. J.D. Watts, J. Gauss and R.J. Bartlett, "Coupled-Cluster Methods with Non-Iterative Triple Excitations for Restricted Open-Shell Hartree-Fock and Other General Single Determinant Reference Functions. Energies and Analytical Gradients," *J. Chem. Phys.*, submitted.
10. S.A. Kucharski and R.J. Bartlett, "Coupled-Cluster Methods Correct Through Sixth Order," *Chem. Phys. Lett.*, submitted.
11. P.G. Szalay and R.J. Bartlett, "Alternative Ansätze in Coupled-Cluster Theory III. A Critical Comparison of Different Methods," *J. Chem. Phys.*, submitted.
12. R.J. Bartlett and J.F. Stanton, "Applications of Post-Hartree-Fock Methods: A Tutorial," in *Reviews in Computational Chemistry*, Vol. 4, eds. D. Boyd and K. Lipkowitz, submitted.
13. S.R. Gwaltney and R.J. Bartlett, Comment on "The relation between Intensity and Dipole Moment for Bending Modes in Linear Molecules," *J. Chem. Phys.*, submitted.

## **V. Invited Presentations (1992)**

December, 1992 — University of Virginia, Charlottesville

November, 1992 — Workshop on Current Trends in Computational Chemistry, Jackson State University, Jackson, MS

July, 1992 — Università Degli Studi Di Bologna, Bologna, Italy

July, 1992 — International Academy of Quantum Molecular Sciences, Menton, France

July, 1992 — IBM Europe Institute, Oberlech, Austria

March, 1992 — Emory University, Atlanta — "Cherry L. Emerson Lecturer"

## **VI. Students Supported**

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